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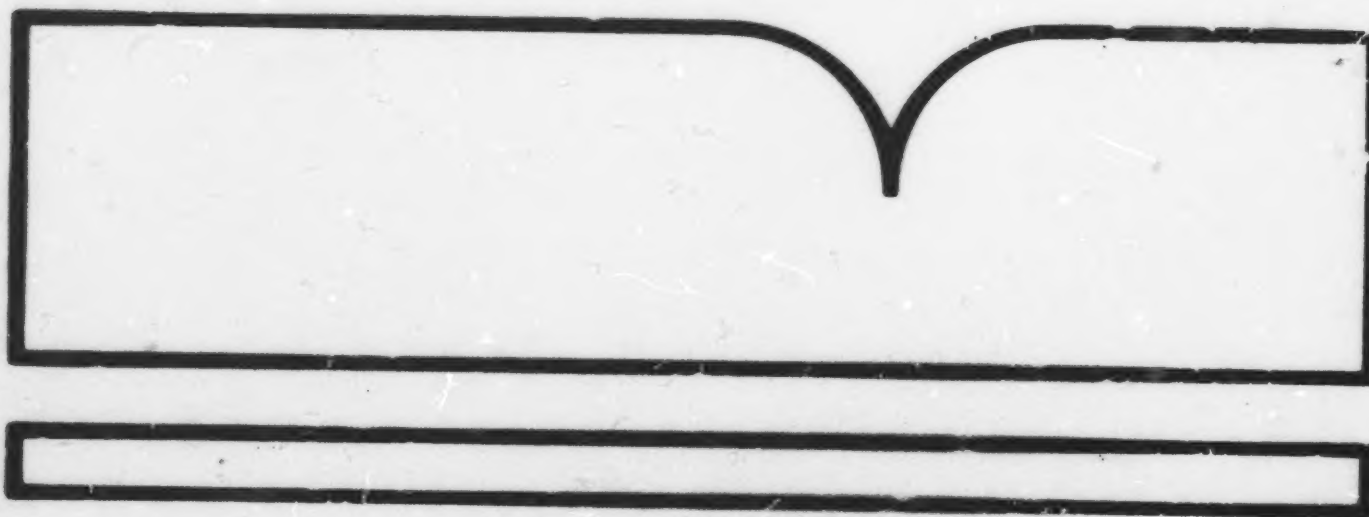
Photolysis of Octachlorodibenzo-P-Dioxin on Soils
Production of 2,3,7,8-TCDD

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PHOTOLYSIS OF OCTACHLORODIBENZO-P-DIOXIN ON SOILS: PRODUCTION OF
2,3,7,8-TCDD

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ABSTRACT

Photolysis of octachlorodibenzo-p-dioxin (OCDD) on soils results in production of the lower chlorinated dibenzo-p-dioxins, notably 2,3,7,8-tetrachloro-dibenzo-p-dioxin (2,3,7,8-TCDD), 1,2,3,7,8-pentachlorodibenzo-p-dioxin (1,2,3,7,8-PCDD) and three hexachlorodibenzo-p-dioxin isomers substituted at the 2,3,7,8-positions. Photodechlorination is favored at the lateral positions for the H₆CDD and P₅CDD congeners, based on the relative yields of the various isomers produced. The mean depth of photolysis of OCDD in the two soils examined varied between 0.06 and 0.13 mm.

INTRODUCTION

Octachlorodibenzo-p-dioxin (OCDD) is a contaminant of the widely used wood preservative pentachlorophenol (PCP), occurring at concentrations ranging from 500 mg/kg to 1500 mg/kg in the technical product¹. Contamination of soils by these compounds has occurred in many areas where PCP has been used, particularly at lumber mill sites. Although the toxicity of OCDD is lower than that of many of the other congeners, the potential exists for conversion of OCDD to the lower chlorinated dioxins, which may result in an overall greater toxicity. Dechlorination occurring predominantly at the 1,4,6,9 positions will result in formation of the highly toxic tetra-, penta-, and hexa-chlorinated dibenzo-p-dioxins. Alternatively, dechlorination at the 2,3,7,8 positions will give products that are less toxic.

OCDD absorbs sunlight and undergoes photolysis to lower chlorinated products. Conflicting results have been published on whether this dechlorination occurs predominantly at the 2,3,7,8 or at the 1,4,6,9 positions, and appears to depend on whether OCDD is dissolved in solution or sorbed on a surface. In solution, Buser² observed that photoreduction occurs primarily at the lateral (2,3,7,8) positions. Irradiation of OCDD gave predominantly 1,2,3,4,6,7,9-heptachlorodibenzo-p-dioxin. Additional work by Dobbs and Grant³ using two hexachlorodibenzo-p-dioxin demonstrated that photodechlorination in solution occurred primarily at the lateral positions. Photoreduction to 2,3,7,8-TCDD, although observed, was a very minor reaction.

Alternatively, Lamparski and coworkers⁴ observed that irradiation of wood treated with OCDD containing pentachlorophenol primarily gave peri, rather than lateral reduction. In a later publication, Nestrick and coworkers⁵ also report the striking observation that, although 2,3,7,8-TCDD is the most photolabile of the 22 TCDD's in solution, it is the most stable TCDD isomer when irradiated as a thin film on glass. Although not a rigorous quantum yield comparison because of the lack of quantitation of light absorption by the various dioxin congeners, they did provide data that suggest that the photochemistry of chlorinated dibenzo-p-dioxins may be different on dry surfaces than in solution.

Our research was designed to determine the degree to which the toxic 2,3,7,8-chlorinated congeners are formed on irradiation of OCDD on soils in relation to the total amount of the various tetra-, penta-, and hexa-chlorinated congeners produced.

EXPERIMENTAL

Two soils were used for these studies. The first was a northeastern Montana soil (2.2% organic matter; 50% sand, 28% silt, 22% clay) and the second was a southern California soil (Tajunga) (0.49% organic matter; 81% sand, 14% silt, 4% clay) obtained as a gift from Dr. Walter Farmer at the University of California-Riverside. Each was air dried and passed through a 0.04 mm sieve prior to treatment with OCDD. Stock OCDD solution (50 mg/L) (Cambridge Isotopes, Cambridge Mass.) was diluted in methylene chloride and mixed with the soils. The methylene chloride was removed by rotary evaporation. For one set of each soil, ethyl oleate was added to the methylene chloride solution at a rate to give 0.1% ethyl oleate of the soil weight used for the irradiations. The solvent was removed by rotary evaporation and the soils were used without further treatment.

The soils were spread evenly on the petri dishes and covered with polyethylene film secured with a rubber band. The OCDD photodechlorination experiments were conducted with 10 mg/kg concentrations and at a depth of 0.25 mm using 3 g of soil for each petri dish. The mean photolysis depths were determined using 2 mg/kg concentrations. Depth was calculated from the weight of the soil, the bulk density of the soil, and the surface area of the petri dishes.

The soils contained in the petri dishes were exposed to a light bank of 16 Westinghouse FS40 sunlamps, which produced maximum intensity at 310 nm. The distance between the lamps and the soil surfaces was 20 cm. The air temperature was maintained at 30°C by a series of fans. Homogeneity of the light intensity for each sample was established using a Spectroline uv intensity meter (280-320 nm). Dark controls were covered with aluminum foil and placed underneath the lamps. No significant loss of OCDD was observed and, except for the same amount of H₇CDD as observed in the nonirradiated samples, no lower chlorinated dioxins were observed. Samples were taken at 0, 5, 10 and 20 days.

For each of the samples, a 1.0 g portion was jar extracted on a shaker for four hours using hexane/methanol (80:20). ¹³C-labelled 2,3,7,8-tetra-, penta-, hexa-, hepta-, and octa-chlorinated dioxin internal standards were added to the samples prior to extraction and used for all quantitation. The extracts were passed through a traditional dioxin cleanup column (acidic and basic silica gel and acid alumina) and concentrated to a final volume of 50 uL in tetradecane. The extracts were analyzed using high

resolution gas chromatography - low resolution mass spectrometry using a 60 m x 0.25 mm DB-5 fused silica capillary column and a Finnigan 4500 mass spectrometer in SIM mode (EPA Method 8280). Qualitative and quantitative confirmation of the 2,3,7,8-substituted tetra- through hepta-chlorinated dioxin isomers was obtained by separation on a 60 m x 0.25 mm SP-2331 fused silica capillary column. Duplicates of samples were analyzed on day 20 samples. The agreement of duplicates in each case was within 15%.

RESULTS AND DISCUSSION

Depth of Photolysis of OCDD

The photolysis of chemicals on soils generally does not follow first order kinetics, in part because of the strong light attenuating effect of soils. Chemicals may become photochemically shielded inside particles near the surface or be shielded simply due to a bulk attenuation effect. Evidence for the inner particle effect was provided by Zepp and Schlotzhauer⁷ who demonstrated that the rate of direct photolysis of chemicals sorbed on suspended sediments is dependent on the time that the chemicals were allowed to equilibrate with the suspended sediments. They observed that longer equilibration times resulted in a photochemically protected fraction of the chemical, which had presumably migrated to the interior of the particles.

For chemicals that move slowly in the soil column relative to photolysis, the plots of average concentration versus time indicate a rapid initial loss, followed by a nearly complete cessation of observable loss. This result allows an experimental method to be developed for assessing the mean photolysis depth of chemicals in soils. This method involves the irradiation of dilute concentrations of a photolabile chemical on a soil sample of known depth. Loss of that chemical occurs until it is no longer photochemically available. The mean photolysis depth is defined as the depth of the soil multiplied by the fractional loss of the chemical at the point where further photochemical loss is no longer observed. Because of the heterogeneity of soils, this depth represents an average of depths, since some molecules may be protected at sites within a few microns of the surface, while light may penetrate many times the mean photolysis depth at other microsites and cause phototransformations. Figs. 1 and 2 show the rate of loss profiles for OCDD on the two soils used in this study.

For the Tajunga soil, the calculated photolysis depths are 0.13 mm and 0.12 mm for the 0.31 mm and 0.62 mm deep soils, respectively. For the Montana

Fig.1 Photolysis of OCDD on Montana soil

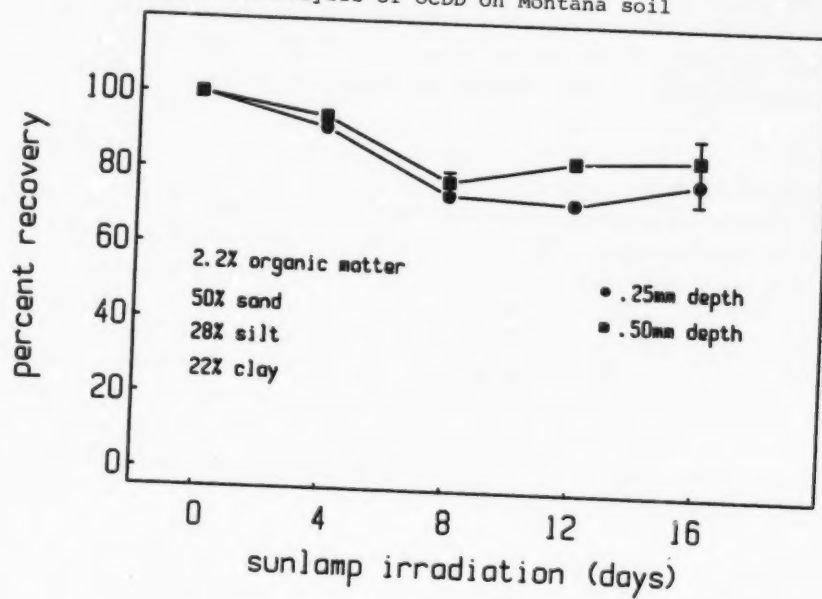
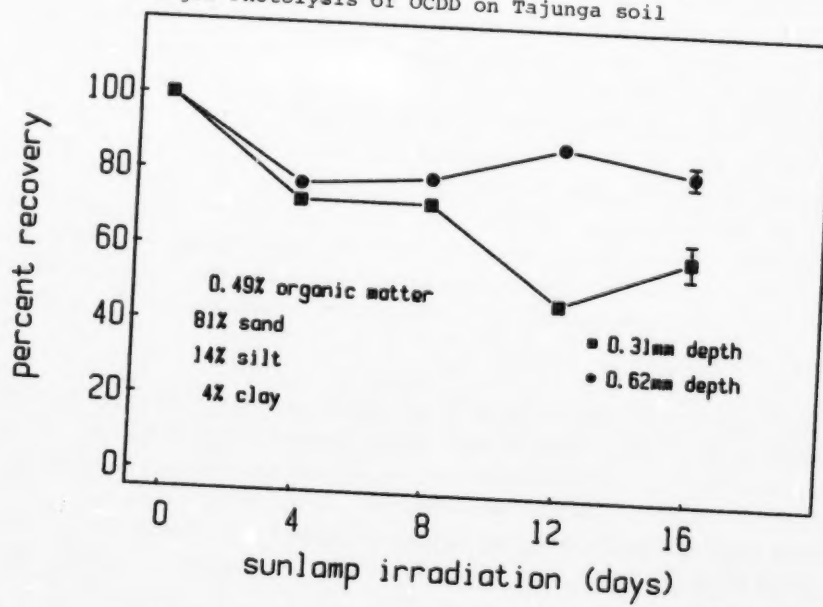


Fig.2 Photolysis of OCDD on Tajunga soil



soil, the calculated mean photolysis depths are 0.062 mm and 0.090 mm for the 0.25 mm and 0.50 mm deep soils, respectively. These depths are indeed shallow, and demonstrate the strong attenuation of light by the soils. These soils did not contain solvents such as ethyl oleate which may increase the movement to the surface and thus the apparent mean photolysis depth.

Photoreduction of OCDD on soil

OCDD was irradiated on both soils with and without added 0.1% ethyl oleate. Ethyl oleate was added as a hydrogen source, which potentially may act to promote photodechlorination reactions. The results on both soils with and without the ethyl oleate are remarkably similar (Table 1-4). Approximately 30 to 45% of OCDD was lost under these irradiation conditions in all of the experiment by day 5 of the irradiation. No significant further loss of the OCDD was observed following 10 additional days of irradiation. Loss of OCDD on the Tajunga soil was greater than that on the Montana soil, in agreement with the mean depth of photolysis results discussed above. The 0.1% ethyl oleate had no observable effect on loss of the OCDD.

Photodechlorination was observed in all of the soils, producing the lower chlorinated dioxins. Approximately 10 to 30% of the lower chlorinated congeners were produced from the immediate higher chlorinated congeners. Although additional OCDD loss was not observed after day 5 of the irradiation, a trend towards increasing levels of the lower chlorinated dioxins was observed on the Montana soil. This trend was not observed for the Tajunga soil. The concentration of the lower chlorinated dioxins did not show an observable loss, however, in any of the soil irradiations between day 5 and 15. This is surprising, since the original molecule had to have been exposed to the radiation for conversion to the lower chlorinated isomer, yet a substantial protecting effect is apparent for the photoproducts. Also, it is apparent that the majority of OCDD that was lost on soils did not appear as dechlorination products. This points to the fact that other photochemical pathways are prevalent in the photolysis of OCDD on soils.

Photoreduction of OCDD to H₇CDD did not occur preferentially at the peri or the lateral positions. Both of the H₇CDD isomers were found in approximately the same concentrations, although the laterally reduced product (1,2,3,4,6,7,9-H₇CDD) was observed in slightly higher concentration. Of the ten H₆CDD isomers, three are substituted in the 2,3,7,8-positions. This proportion also is observed for the yield of the

Table 1. Photodechlorination of octachlorodibenzo-p-dioxin on Montana soil under FS40 lamps

Dioxin	Days of Exposure			
	0	5	10	20*
octa	10500 ng/g	6550 ng/g	7250 ng/g	6940 ng/g
hepta total (1234678)	34 14	190 81	220 97	253 109
hexa total (123478) (123678) (123789)	(<0.12)	33 2.2 2.7 3.4	45 4.3 3.8 5.0	75 6.1 6.1 7.0
		8.3	13	19
penta total (12378)	(<0.13)	4.3 1.5	10.1 2.1	19 5.2
tetra total (2378)	(<0.087)	0.55 (<0.34)	0.64 0.39	1.5 0.86

*average of duplicate samples

Table 2. Photodechlorination of octachlorodibenzo-p-dioxin on Montana soil under FS40 lamps with 0.1% ethyl oleate

Dioxin	Days of Exposure			
	0*	5	10	20*
octa	9845 ng/g	6800 ng/g	4750 ng/g	7000 ng/g
hepta total (1234678)	36 15	214 90	193 86	269 115
hexa total (123478) (123678) (123789)	(<0.12)	36 3.0 2.6 3.5	52 5.4 5.4 3.7	67 6.7 5.5 6.7
		9.1	15	19
penta total (12378)	(<0.13)	7.0 2.1	11 2.0	19 4.9
tetra total (2378)	(<0.087)	0.57 0.34	(<0.35)	1.5 0.66

*average of duplicate samples

Table 3. Photodechlorination of octachlorodibenzo-p-dioxin on Tajunga soil under FS40 lamps

Dioxin	Days of Exposure			
	0	5	10	20*
octa	9580 ng/g	5510 ng/g	5750 ng/g	5570 ng/g
hepta total (1234678)	36 14	293 132	304 140	318 146
hexa total (123678+123478) (123789)	(<0.24)	58 11 — 18 7.1	67 13 — 21 7.9	75 15.2 — 24 8.7
penta total (12378)	(<0.32)	14.8 4.4	12.0 3.4	15.6 4.6
tetra total (2378)	(<0.042)	1.5 0.94	1.5 1.1	2.0 1.2

*average of duplicate samples

Table 4. Photodechlorination of octachlorodibenzo-p-dioxin on Tajunga soil containing 0.1% ethyl oleate under FS40 lamps

Dioxin	Days of Exposure			
	0	5	10	20*
octa	9365 ng/g	6260 ng/g	6920 ng/g	6080 ng/g
hepta total (1234678)	42 17	305 96	233 102	340 116
hexa total (123478) (123678) (123789)	(<0.27)	50 2.7 — 8.7 2.2 3.8	49 3.5 — 11 3.7 3.7	53 3.9 — 12 3.6 4.8
penta total (12378)	(<0.43)	6.6 0.88	7.7 2.4	7.9 1.9
tetra total (2378)	(<0.050)	0.60 0.25	0.70 0.39	0.63 0.41

*average of duplicate samples

photoproducts. Of the fourteen P₅CDD isomers, only one is substituted at the 2,3,7,8-positions, yet the proportion of this toxic isomer is 20 to 35% in the four soils at day 15. This represents a significant enhancement over that expected based simply on the isomer distribution. Finally, 2,3,7,8-TCDD was observed at a level 0.4 to 1.2 ng/gm. Approximately half of the total T₄CDD dioxin yield is 2,3,7,8-TCDD. Because 22 T₄CDD isomers exist, this is a substantial enhancement and indicates that peri rather than lateral photodechlorination is predominating in the observed yield.

The relative proportions of the observed photoproducts can potentially be affected by two factors. First, the observed distribution could reflect a more rapid photolysis of individual congeners, leaving the more stable congeners. For example, 2,3,7,8-TCDD was shown to be the most photochemically stable of all of the T₄CDD isomers on a glass surface by Nestricks and coworkers⁵, which may explain the enhanced levels of this isomer on the soils. Second, the photodechlorination may preferentially proceed to give the observed product ratios, which are maintained. Although not conclusive, the data supports the second possibility more strongly, since the ratios of the total quantity of dioxins divided by the quantity of the 2,3,7,8-substituted isomers within each chlorination level remain relatively constant from day 5 to day 20.

In octane solution, photodechlorination occurred predominantly at the lateral position (Table 5), as was observed by Dobbs and Grant³ and Buser². The proportion of lateral versus peri photodechlorination is due to the

Table 5. Photodechlorination of octachlorodibenzo-p-dioxin in isooctane under FS40 lamps

Dioxin	Hours of Exposure		
	0	4	12
octa	25900 ng/mL	14400 ng/mL	3500 ng/mL
hepta total	30	7560	6360
(1234678)	8.3	163	110
hexa total	(<0.47)	18	2130
(123678)			1.6
penta total	(<0.28)	9.3	24
tetra total	(<0.11)	(<1.9)	(<3.4)

preferential photochemical reduction at the lateral position, since the difference in rates of loss of the two isomers is not sufficient to account for the substantial difference in yield². Only a very small quantity of the 2,3,7,8-substituted H₆CDD isomer was observed and no 2,3,7,8-substituted P₅CDD or T₄CDD was observed. Photodechlorination to the H₇DD isomers accounts for a majority of the loss of OCDD (~67%) at four hours of irradiation, which also indicates that the solution photochemistry is distinctly different than that observed in the sorbed phase. The reasons for this difference are, however, unknown.

CONCLUSION

These results indicate a substantial difference in the photochemistry of OCDD at the soil surface, compared to that observed in solution. In solution, only very small amounts of the toxic 2,3,7,8-substituted dioxins are formed; at the soil surface, formation of the toxic 2,3,7,8-substituted congeners is preferred. Although the depth of photolysis is shallow (0.06 to 0.13 mm) and the conversion to the toxic T₄CDD, P₅CDD and H₆CDD congeners is small (0.5 to 1%), photolysis of OCDD may represent a significant production of these toxic isomers. Further work is presently ongoing to confirm these results in sunlight. Preliminary data indicate similar product distributions in sunlight.

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